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## **SURFACE CHARACTERIZATION OF NANOSTRUCTURED COATINGS: STUDY OF NANOCRYSTALLINE SnO<sub>2</sub> GAS SENSORS**

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### **1. Introduction**

In principle, all the properties of bulk materials can be determined provided that the composition and the structure of the material are sufficiently well defined. But, it is easy to realize that the properties at a solid surface are altered because of the very presence of the surface constituting a fundamental discontinuity. When the size of the solid is decreased down to the nanometer scale, the nanoparticles can be considered as *surfaces in three dimensions* and the relationships between bulk structure and material properties are no longer valid. In nanostructured coatings, the constituent phase or the grain structure may have sizes of the order of 10 nm or less, leading to a high number of atoms either at the external surface or at the grain boundaries. Besides, the material synthesis history and the preparation method of the layers govern the surface structure and the surface composition of coatings. Therefore, precise surface characterization is a strong requirement to control the surface properties and to further improve the nanostructured coating performances.

As a general requirement, the methods used to characterize clean or real surfaces must be sensitive enough to detect the small number of surface atoms. But, when applied to nanostructured materials, the surface characterization techniques must additionally be capable of analyzing a depth significantly smaller than the size of the grain to solely take the surface layer into consideration. Most of the techniques for surface analysis are essentially based on the scattering, absorption or emission of photons, electrons, atoms or ions. But no single technique can provide all necessary information about surface atoms [1].

As an example, the study by Fourier transform infrared (FTIR) surface spectrometry of semiconductor nanostructured thick films used as chemical gas sensors will be discussed. It will be shown that this cost-effective technique allows one to identify the surface chemical species, to test the reproducibility of the surface oxidation state and to determine the type of semiconductivity. In addition, emphasis will be put on the capability of FTIR surface spectrometry to provide information simultaneously on the chemical reactions taking place at the gas-sensing layer interface and on the resulting

variations of the electrical conductivity of the surface layer. Besides, because the gas sensing properties are essentially dependent on the surface reactivity, it will be shown how modifications of the chemical species of the sensor surface can affect the gas detection.

## 2. Surface Analysis

### 2.1. GENERAL CONSIDERATIONS

The definition of a surface is highly subjective. The phenomena to be studied generally define the depth of the surface layer to take into consideration [2]. For example, adsorption only concerns the adsorbed molecules or atoms and the very first atomic layer (monolayer) of the solid. On the contrary, changes in the electrical properties of a semiconductor usually affect over one hundred atomic layers. Therefore, the technique for the analysis of a specific surface phenomenon must be chosen by carefully comparing the thickness of the surface layer that will be perturbed and the depth that the envisaged method can sample. This is not an easy task because this depth mainly depends on the material and on the energy of the probing particles (photons, electrons, atoms or ions). In addition, some techniques can be used at grazing angle of the incident beam instead of normal incidence, thus greatly influencing the depth of sampling [3]. Since different techniques (or eventually the same technique but under different conditions) have different depths of sampling, it must be kept in mind that discrepancies can occur between the results obtained on the same sample by different methods. Moreover, because the characterization technique has to be chosen with respect to the property to be analyzed, the simultaneous study of correlated properties involving the surface layer at different thicknesses seems like trying to "square the circle".

On the other hand, a complete surface characterization should reveal the chemical nature of the surface atoms, their concentrations, their electronic states as well as their arrangements with respect to each other and with respect to the underlying atoms [4]. The thorough investigation of the surface composition and structure should lead to the control of the electronic and chemical properties of this surface. However, no single technique can provide both structural and chemical complete information.

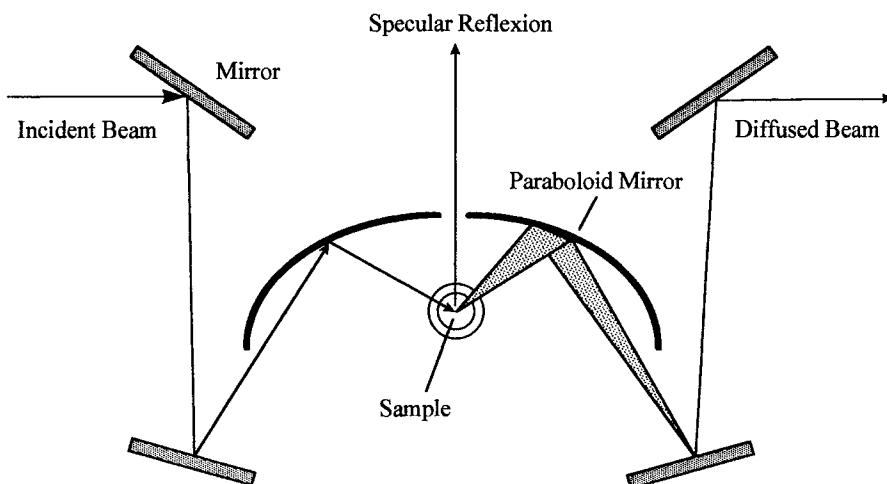
Despite all these difficulties, the critical need for the control of materials surfaces, and particularly of nanomaterials surfaces, leads to a constant development and improvement of instrumentation for surface analysis. This paper does not intend to review the techniques used for the study of surface structure and chemical composition. Several books describe these methods with respect to their field of interest [2-5] such as X-ray photoemission spectroscopy (XPS or ESCA), extended X-ray absorption fine structure (EXAFS), electron energy loss spectroscopy (EELS), Auger electron spectroscopy (AES), atomic force microscopy (AFM) and scanning tunneling microscopy (STM), ion-scattering spectroscopy (ISS), to name only a few. Among the methods that do not involve probing particles, let us quote: thermal desorption

spectroscopy (TDS) and temperature programmed desorption (TPD). Instead, the emphasis will be put on the possibilities offered by Fourier transform infrared (FTIR) spectrometry.

Although FTIR spectrometry is not usually considered as a surface-sensitive technique, under particular configurations it can be a high-performance tool for the surface analysis of nanosized powders [6-7]. When non-transparent materials have to be studied, the transmission mode is no longer appropriate. Then, the infrared radiation diffused by the sample becomes the most relevant effect to be investigated. Diffuse reflectance infrared Fourier transform spectrometry (DRIFTS) allows the analysis of films and coatings deposited on absorbing substrates and of the surface layer of bulk samples as well.

## 2.2. DIFFUSE REFLECTANCE SPECTROMETRY

In 1978, Fuller and Griffiths [8] published an optical arrangement for the measurement of diffuse reflectance infrared spectra of powdered samples. The schematic design is represented in Figure 1. An off-axis paraboloid mirror (focusing mirror) is used to focus the infrared beam onto the sample whereas an on-axis paraboloid mirror (collecting mirror) collects the radiation diffusely reflected from the sample. The specularly reflected radiation is eliminated through a hole drilled on the axis of the collecting mirror. The recent attachments for diffuse reflectance measurements are still based on this original design.



*Figure 1.* Optics for the diffuse reflectance infrared Fourier transform spectrometry

The theory of the diffuse reflectance is extremely complex and the determination of the penetration depth of the infrared radiation into the sample is not straightforward. Many theories have been proposed based on various models, each of them being valid under a specific set of conditions. A critical discussion of different theories can be found in [9] for example. Without going into details, it should be borne in mind that the diffuse reflectance is highly dependent upon the nature of the absorbent (refractive index, particle size, particle shape and particle size distribution etc) and upon the surface roughness. Note that a very smooth surface is not appropriate for such analysis because the specular reflectance is very intense whereas the diffuse reflectance becomes negligible. But, in any case, it must be clearly realized that, whatever the sample, a diffuse reflectance spectrum not only contains information on the surface species (very first atomic layer) but also on the bulk. To discriminate the bands due to the surface species from those originating from the bulk vibrations, a specific cell called environmental chamber must be attached to the diffuse reflectance accessory. Like in the case of transmission measurements [6-7, 10], this cell allows a thermal treatment of the sample under vacuum or controlled pressures of gases. Indeed, a thermal treatment of the sample under dynamic vacuum clears the surface from impurities, thus allowing the characterization of the surface chemical species such as hydroxyl groups, carbonates and hydrocarbon residues etc. In addition, selected probe-molecules can be purposely adsorbed on the film/coating surface to identify possible surface reactive sites. Under those conditions, the very first atomic layer of a film/coating can be fully characterized in the same way as that of a nanosized powder [6-7]. Moreover, the gas-surface interactions can be followed *in situ* as a function of the temperature and/or the gas pressure.

When a powdered sample is mixed with a nonabsorbing salt, such as potassium bromide, the infrared radiation can propagate into the salt grains and then undergoes several external and internal reflections before it emerges from the sample. In this case, the contribution of the surface species to the diffuse reflectance spectrum is relatively larger than in the case of the same powder studied in transmission mode. Obviously when the sample to be analyzed is a thick film, the diffuse reflection is limited to the external surface layer. As a consequence, the intensity of the bands originating from the surface species is weaker. This is the reason why the surface study by diffuse reflectance of thick films or bulk samples can only be successfully performed with highly sensitive infrared detectors. However, the nanocrystalline structure of films and coatings leads to an increase of the external surface area, thus facilitating their surface analysis by DRIFTS.

### 3. Semiconductor Coatings and Thick Films

When the material to be analyzed is a semiconductor, FTIR spectrometry can bring additional information on the electrical conductivity variations. According to the Drude-Zener theory [11], the infrared energy absorbed by a semiconductor is essentially due to surface states and to free carriers. Therefore, the absorbed infrared energy is related to the electrical conductivity of the semiconductor. Obviously, the more the infrared energy

is absorbed by the sample, the less it is scattered. In other words, a decrease of the infrared energy diffused by a semiconductor means an increase of its electrical conductivity provided that the surface states are not strongly modified.

Because of the optical properties of semiconductors and metals, it is not expected that DRIFTS can sample more than a few nanometers deep in such materials [8]. The surface layer corresponding to these few nanometers may actually represent the depletion layer in a semiconductor. For example, in tin oxide the depletion layer is estimated around 3 nm [12] which is probably close to the analyzed depth of a  $\text{SnO}_2$  thick film by DRIFTS. Keeping in mind that DRIFTS allows the analysis of the very first atomic layer and the study of the gas-surface interactions thanks to the use of the environmental chamber, it can be easily realized that, with this technique, the modification of the first atomic layer and its consequence on the electrical conductivity can be simultaneously followed under the same environment. This is the basis of fundamental studies of gas detection mechanisms in semiconductor-based sensors.

To clearly explain the dual possibility of DRIFTS, let us consider a semiconductor gas sensor based on tin oxide. The sensor is usually fabricated from a paste, consisting of a dispersion of the tin oxide particles in an appropriate solvent, deposited over a substrate (e.g. an alumina tile) and then fired to ensure a network of interconnected tin oxide grains [13]. It must be noted that preventing undesirable nanoparticle agglomeration during dispersion of the nanopowder and during further thermal treatment of the layers requires a state-of-the-art knowledge in surface chemistry. Depending on the temperature, oxygen adsorption onto the surface of these grains causes the removal of electrons from the conduction band and therefore a decrease of the electrical conductivity. An electron-depleted zone (space charge layer) is thus created at the surface and it generates a potential barrier between neighboring grains. When a reducing gas is adsorbed on the tin oxide surface, electrons are injected into the conduction band, decreasing the depth of the space charge layer and increasing the electrical conductivity. These changes in the electrical conductivity translate into variations of the background absorption of the sample in the infrared range. Note that, when the tin oxide particle size is considerably greater than the depth of the depletion layer, the electrical conductivity is controlled by the grain boundaries. But, when the sensing layer is constituted of nanoparticles, the depth of the depletion layer becomes comparable to the particle radius and then the electrical conductivity is controlled by the grains themselves. Therefore, the oxygen adsorption will result in fully depleted grains and to a high resistance of the material. As a consequence, the sensitivity of the sensor is increased and the effects on the background infrared absorption of the sample become more pronounced. As previously explained, a gas adsorption or ionosorption on the  $\text{SnO}_2$  first atomic layer has consequences on several hundreds of atomic layers in depth. Because the chemical reactions occurring at the very surface can be studied by DRIFTS and because the variations of the electrical conductivity generated by these chemical reactions are related to the variations of the infrared energy diffused by the sample, DRIFTS appears as a very relevant tool for the study of the gas detection mechanism in a semiconductor-based sensor.

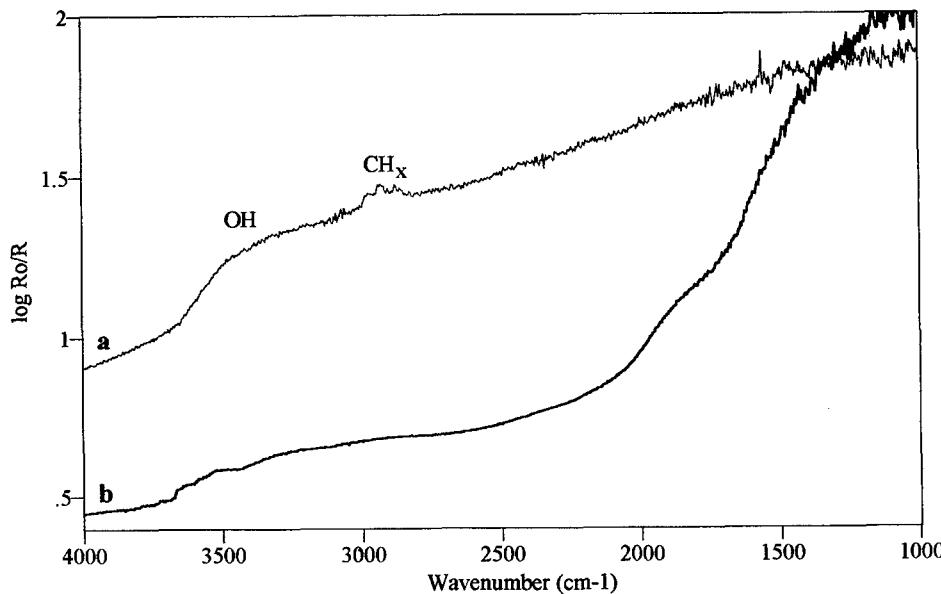
#### 4. Study of a nanocrystalline tin oxide-based sensor

The sensors considered in the following are fabricated from nanosized tin oxide powder [13] obtained by laser evaporation of a tin oxide rod under specific conditions [14]. The size of the tin oxide primary particles is 8 nm and these particles are shown not to significantly grow during the firing step of the sensing layer preparation [13]. These sensors show an excellent sensitivity toward carbon monoxide in presence of oxygen. Details on the sensors fabrication and on their electrical characteristics can be found in [13].

##### 4.1. DETERMINATION OF THE TYPE OF THE SEMICONDUCTOR BY DRIFTS

Even though it is well known that tin oxide is a n-type semiconductor under standard conditions, the following procedure illustrates how it is possible to determine the type of the semiconductivity by DRIFTS without using any electrode.

A non-fired sensor without electrode, that is the sensing thick film deposited onto the alumina tile and dried at 373 K, is placed in the DRIFTS environmental chamber. The infrared spectrum recorded at room temperature in air is presented in Figure 2a.



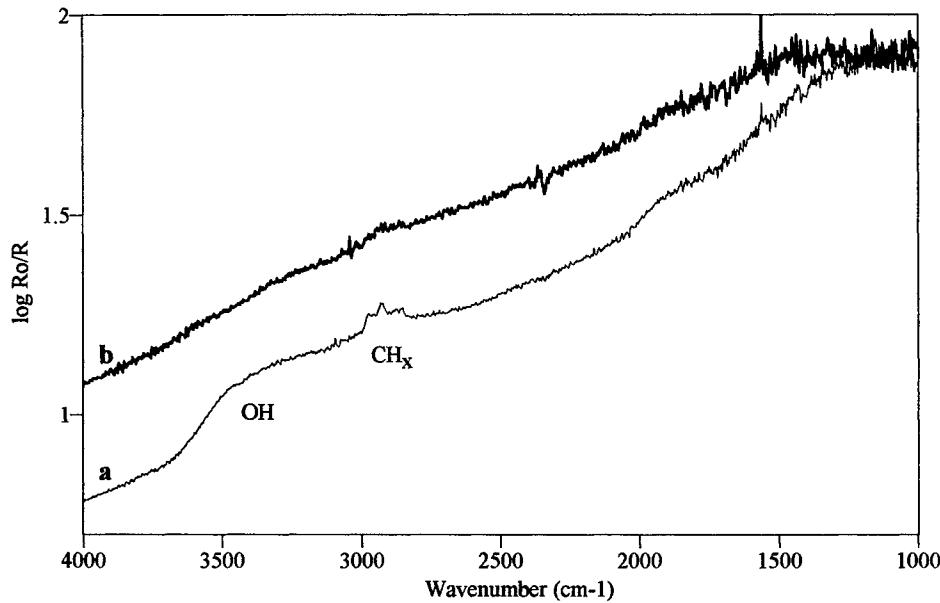
*Figure 2.* Diffuse infrared spectra of the n-SnO<sub>2</sub>-based sensor:  
a) at room temperature under atmosphere; b) after heating at 673 K under atmosphere.

The broad band centered around  $3300\text{ cm}^{-1}$  has been proved to correspond to atmospheric molecular water adsorbed on the Sn-OH surface hydroxyl groups [15] whereas the group of weaker bands in the  $3000\text{ cm}^{-1}$  region is due to the  $\text{CH}_x$  groups of the organic binder. When the sensor is heated under atmosphere, the  $\text{CH}_x$  groups are steadily eliminated as well as part of adsorbed molecular water (Figure 2b). But the most important modification of the infrared spectrum of the sensor during the thermal treatment is the decrease of the background absorption. This is due to the oxygen ionosorption on the sensor surface when the temperature increases. As previously explained, the oxygen ionosorption leads to an increase of the depth of the depletion layer, that is to a decrease of the free carrier density. As a consequence, a decrease of the background absorption of the infrared radiation by the free carriers is observed, which is related to the decrease of the electrical conductivity. This is the proof that the sample is a n-type semiconductor. Conversely, when the sensor is heated under dynamic vacuum (Figure 3), the absorption of the sample increases with temperature, thus proving an increase of the electrical conductivity. Indeed, this thermal treatment under vacuum is a reducing treatment and leads to oxygen loss mainly from the surface layer of the sample. Obviously, for a p-type semiconductor, the oxygen ionosorption causes the opposite effect on the background infrared absorption. This simple experiment is therefore an easy and fast method to determine the type of the semiconductor material while avoiding the perturbation which may be caused by the use of metallic electrodes.

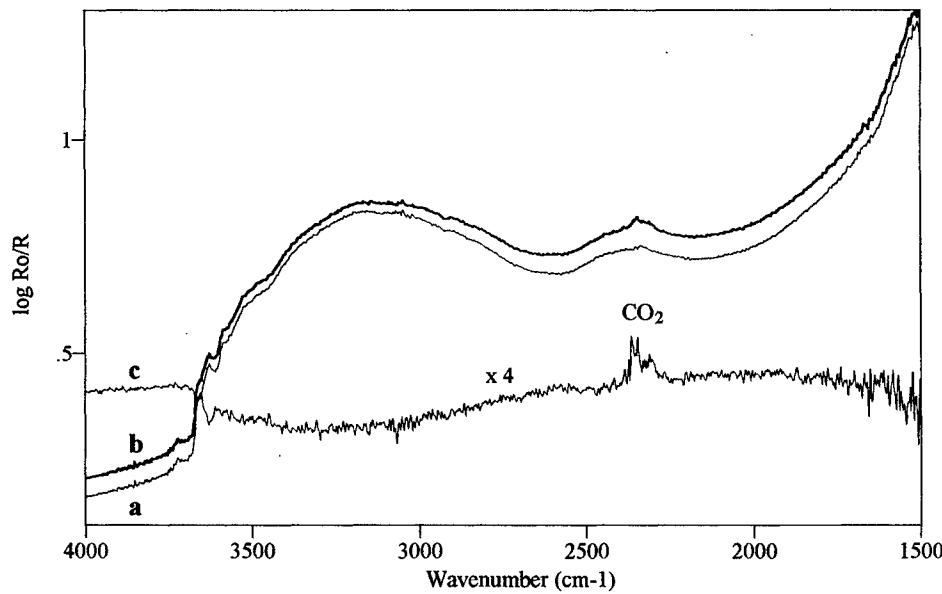
#### 4.2. GAS DETECTION MECHANISM

Various infrared experiments have been performed on the sensing layer described above to simulate the gas detection by the semiconductor-based sensor. As a first step, the pretreatment conditions of the sensor [13] are reproduced by heating the sensing layer at 673 K under 50 mbar of oxygen and then cooling it to the chosen operating temperature while still under oxygen. As previously explained, this procedure decreases the electrical conductivity because oxygen adsorbs on the surface as different ionized species. By studying the original nanosized tin oxide powder, these species have been identified as mainly  $\text{O}^-$  and  $\text{O}_2^-$  [15] whose relative amount depends on the temperature [16]. Note that the adsorption of oxygen onto the as-received nanopowder surface allows one to identify defect sites where molecular oxygen is preferentially adsorbed at room temperature. These defect sites are destroyed by annealing under oxygen [15]. From the electrical measurements, it has been determined that this undoped sensor is sensitive toward reducing gases at an operating temperature ranging from 373 to 773 K [13] with two sensitivity local maxima at 393 K and 623 K. The experiments described below have been performed at these latter temperatures.

After the thermal pretreatment under oxygen, the sensor surface is subjected to 10 mbar of carbon monoxide (CO) at 623 K in presence of oxygen for 10 minutes. The electrical conductivity increases, which on the infrared spectrum translates into an increase of the background absorption (Figure 4a,b). Moreover, by looking closer at the



*Figure 3.* Diffuse infrared spectra of the n-SnO<sub>2</sub>-based sensor:  
a) at room temperature under vacuum; b) after heating at 673 K under dynamic vacuum.



*Figure 4.* Diffuse infrared spectra of the n-SnO<sub>2</sub>-based sensor at 623 K:  
a) under 50 mbar O<sub>2</sub>; b) after addition of 10 mbar CO; c) difference spectrum: b-a.  
The Y axis refers to spectra a and b, spectrum c has been translated for clarity sake.

infrared spectra, it is possible to detect the formation of carbon dioxide as shown on the difference spectrum (Figure 4c). Then, the gases ( $O_2$ , CO and the newly formed  $CO_2$ ) are quickly evacuated and a new dose of oxygen (50 mbar) is added for 10 minutes followed by 10 mbar CO. This additions/evacuation sequence is repeated several times and the infrared energy diffused by the sensing layer in the entire wavenumber range scanned by the spectrometer ( $7800-450\text{ cm}^{-1}$ ) is reported versus gas exposures in Figure 5. The variations of the diffuse infrared energy can be related to the sensor response. It can be seen that under oxygen the electrical conductivity of the sensor decreases whereas it increases under CO. This increase can be related to the  $CO_2$  formation observed on the infrared spectra. During the evacuation of all of the gases present in the cell, the sample is reduced as expected from the oxygen desorption and from the removal of ionosorbed oxygen species used for the  $CO_2$  formation. When the sample is again subjected to oxygen, the oxidation state of the surface is totally regenerated.

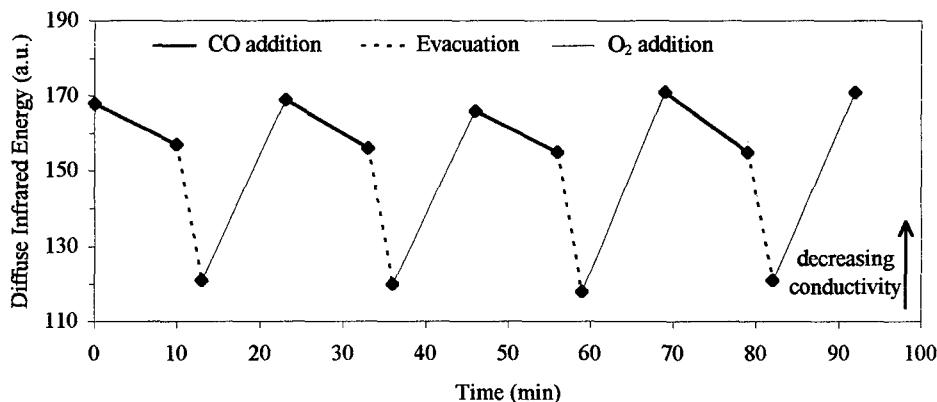


Figure 5. Infrared energy diffused by the n-SnO<sub>2</sub>-based sensor at 623 K versus gas exposures.

In another experiment at 623 K, oxygen was quickly evacuated before CO addition (10 mbar). The introduction of the reducing gas causes a strong decrease of the infrared energy diffused by the sensing layer (Figure 6). Taking into account the detection limits of our system, the formation of  $CO_2$  is either very weak or absent. A rapid evacuation does not lead to significant changes. Whereas the addition of a second CO dose may be responsible for a very slight increase of the electrical conductivity, further evacuation or CO addition is not detected by the sensor. The sensor seems unable to undergo further reduction, thus proving that the nanosized tin oxide particles are totally reduced after the first CO addition. But, when the sensing layer is subjected to oxygen, the recovery is immediate (Figure 6).

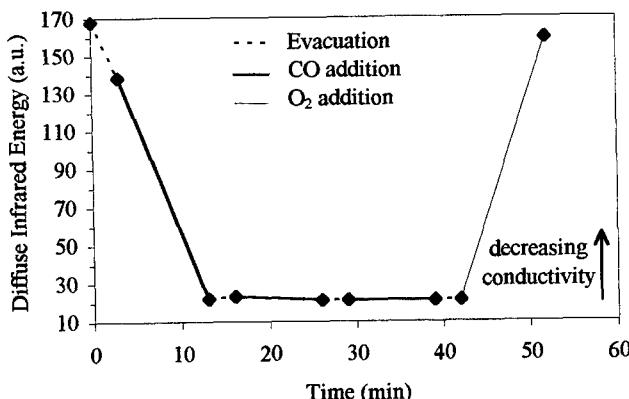


Figure 6. Infrared energy diffused by the n-SnO<sub>2</sub>-based sensor at 623 K versus gas exposures.

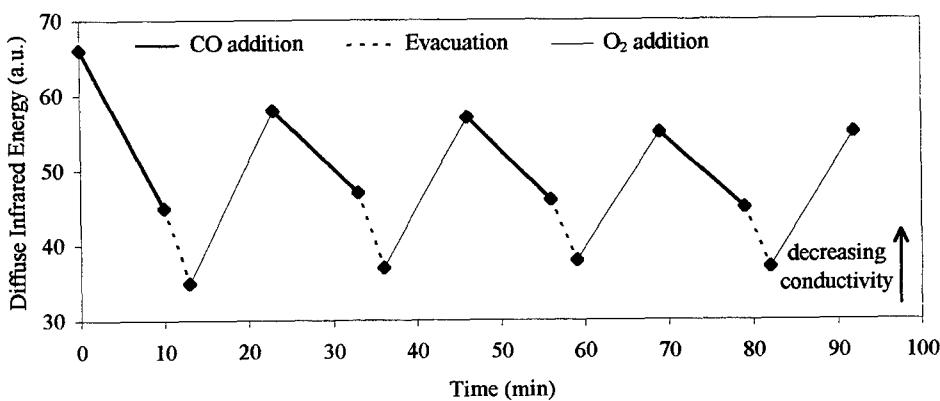


Figure 7. Infrared energy diffused by the n-SnO<sub>2</sub>-based sensor at 393 K versus gas exposures.

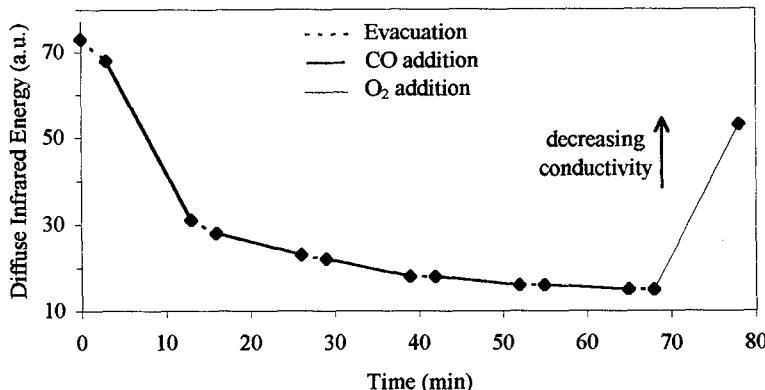


Figure 8. Infrared energy diffused by the n-SnO<sub>2</sub>-based sensor at 393 K versus gas exposures.

The two above experiments prove that the nanostructured tin oxide-based sensor strongly requires an oxygen environment for normal operation. It is amazing how fast the reduction of the nanoparticles can be, thus strengthening the need for oxygen to balance out the complete depletion of the nanoparticles in a reducing atmosphere.

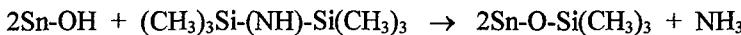
Similar experiments (CO additions in presence or in absence of oxygen) were performed on the same sensing layer at 393 K. The variations of the diffuse infrared energy versus gas exposures are given in Figures 7 and 8. The major difference with the experiments performed at 623 K is that the formation of CO<sub>2</sub> is not observed even in presence of oxygen. This is not completely surprising because this lower temperature should prevent the CO combustion. However, the response of the sensor is far from being negligible and this phenomenon is in good agreement with the electrical measurements showing a sensitivity local maximum around 393 K [13]. We tentatively explain the sensor response toward CO, without formation of CO<sub>2</sub>, by the adsorption of the CO molecules on the sensing layer surface. Indeed, this adsorption, only possible around room temperature, should modify the thickness of the depletion layer and therefore the electrical conductivity of the semiconductor material. By comparing the results obtained at 393 K and at 623 K, we note that the recovery of the oxidation state of the sensor surface is slower at 393 K, and that the total reduction of the sensor by subsequent CO additions in absence of oxygen is slower as well (Figure 8).

With these DRIFTS experiments, we have correlated the variations of the electrical conductivity of the sensing layer with the oxidation of carbon monoxide into carbon dioxide on the sensor surface. Moreover, in agreement with the electrical conductivity measurements, we have demonstrated that, at low temperature, the response of the SnO<sub>2</sub>-based sensor is not due to the CO combustion. We have also produced the proof that the presence of oxygen is essential for the reproducibility of the sensor response whatever the operating temperature.

#### 4.3. MODIFICATION OF THE SURFACE SPECIES AND CONSEQUENCES ON THE SENSOR RESPONSE

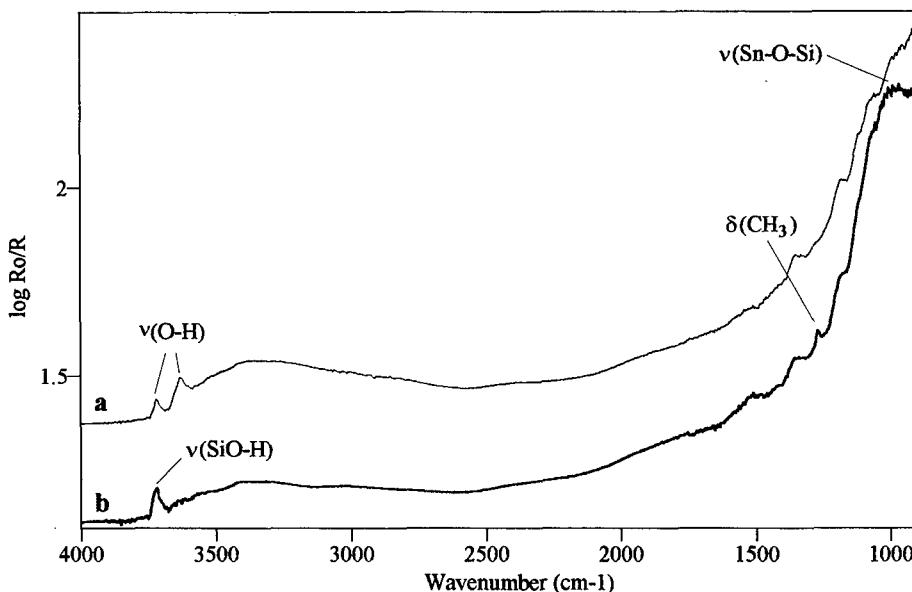
The gas detection mechanism is essentially a surface phenomenon generating modifications in the depletion layer of the semiconductor material. Besides, the surface properties of a film or coating may be changed when organic substances are adsorbed [17]. Therefore, when the surface chemistry of the sensing layer is modified, consequences should be observed on the sensor response. For example, the response toward CO is mainly dependent on the oxygen ionosorbed species but this response can be strongly affected by the presence of humidity. The hydroxyl groups present on all metal oxide surfaces are known to play an important role in the surface properties since they can act as adsorptive or reactive sites [17]. Particularly, humidity interacts with these OH groups although the precise mechanism correlating the chemical interactions and the electrical response of the semiconductor is not completely understood [18]. Therefore, chemical modifications of surface hydroxyl groups are expected to change the sensor sensitivity toward humidity.

To check this hypothesis, hexamethyldisilazane (HMDS) is grafted on the hydroxyl groups of the tin oxide surface. A thorough infrared study of the grafting mechanism has been previously performed on the tin oxide nanopowder [19] which is used to fabricate the sensing layer. HMDS reacts with the surface OH groups according to the following reaction:



When the grafted sample undergoes a subsequent oxidation, the  $\text{Si}(\text{CH}_3)_3$  groups prove to transform into new Si-OH groups linked to the tin oxide surface [19]. Obviously, these newly formed Si-OH groups do not have the same acid-base reactivity as that of the Sn-OH groups on the original tin oxide surface. Therefore, their reactivity toward water molecules should be different.

The surface of the sensing layer has been modified according to a procedure previously described [19-20]. The diffuse reflectance spectra of the sensing layer before HMDS grafting and after HMDS grafting followed by a thermal treatment under oxygen at 673 K are presented in Figure 9.



*Figure 9.* Diffuse infrared spectra of the n- $\text{SnO}_2$ -based sensor:  
a) after oxidation at 673 K; b) after HMDS-grafting followed by an oxidation at 673 K.  
The Y axis refers to spectrum a, spectrum b has been translated for clarity sake.

After the grafting and the oxidation (Figure 9b), the band at  $3630\text{ cm}^{-1}$  assigned to the  $\nu(\text{OH})$  stretching vibration of Sn-OH surface groups on the tin oxide grains [15] has completely disappeared because of the reaction of the corresponding OH groups with HMDS. The band at  $3717\text{ cm}^{-1}$ , also assigned to  $\nu(\text{OH})$  of surface groups, is not strongly modified by the grafting. This band that does not exist in the spectrum of the pure  $\text{SnO}_2$  nanosized powder may be due to OH groups remaining from the organic binder. After HMDS grafting, the shoulder which appears at  $3726\text{ cm}^{-1}$  on the high-wavenumber side of the  $3717\text{ cm}^{-1}$  band is assigned to the  $\nu(\text{OH})$  stretching vibration of new Si-OH surface groups. The sharp band at  $1270\text{ cm}^{-1}$  is due to the  $\delta_s(\text{CH}_3)$  bending vibration of the  $(\text{CH}_3)$  groups of the grafted HMDS [19]. At lower wavenumbers, the broad band around  $1000\text{ cm}^{-1}$  has been assigned to the  $\nu(\text{Sn}-\text{O}-\text{Si})$  stretching vibration [19]. All of these features prove that HMDS is grafted on the sensor surface and that the oxidation of the grafted species proceeds like on the tin oxide powder surface.

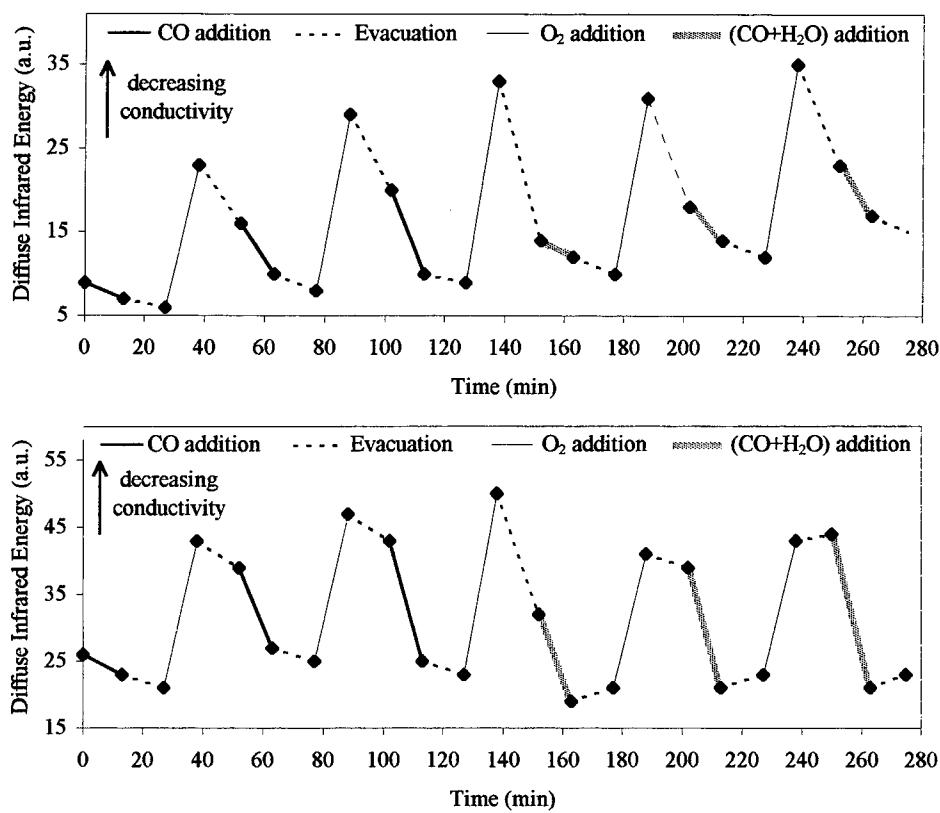


Figure 10. Infrared energy diffused by the n- $\text{SnO}_2$ -based sensor at  $523\text{ K}$  versus gas exposures: top) before grafting; bottom) after HMDS grafting.

To analyze the effects of the surface modifications on the sensor response, the sensitivity of the sensor is tested before and after grafting. The same addition/evacuation sequences are followed in both cases: oxygen addition, quick evacuation, pure carbon monoxide addition, quick evacuation. This sequence is repeated twice and from the forth sequence, carbon monoxide is replaced by a mixture of water vapor and carbon monoxide at increasing H<sub>2</sub>O/CO pressure ratios (10, 20, 40%). The variations of the diffuse infrared energy versus gas exposures is reported in Figure 10. It can be seen that, before grafting (Figure 10a), the presence of humidity strongly affects the sensor response toward CO, whereas after grafting (Figure 10b), the amplitude of the response is stable whatever the humidity level. This experiment clearly demonstrates the importance of the chemical composition of the first atomic layer in the gas detection mechanism.

The different behavior of the non-grafted and grafted sensor toward humidity is explained by the drastic modification of the chemical nature of the surface hydroxyl groups. The Si-OH surface groups formed after HMDS grafting and subsequent oxidation should have an acido-basicity close to that of the OH groups on a silica surface, that is quite different from that of the Sn-OH groups originally on the sensor surface. The constant amplitude of the response toward CO in presence of humidity indicates a stabilizing surface effect by HMDS, which has been already observed on titania [21] but its complete mechanism is still unknown. The Si-OH groups are believed to play an important part in neutralizing the effect of humidity possibly because their amphoteric character gives them equal opportunity to interact with OH<sup>-</sup> and H<sup>+</sup> ions originating from the dissociation of a water molecule.

## 5. Conclusion

Surface studies of materials are generally difficult to perform mainly because the adequacy between the property to be analyzed and the investigation tool is not easily satisfied. Obviously, the difficulty increases in the case of nanomaterials.

Diffuse reflectance infrared spectrometry, often used to analyze the bulk of standard materials, has been demonstrated to be relevant for surface studies of nanostructured films and coatings under particular conditions. The first atomic layer can be characterized as far as the chemical composition of the surface species is concerned. The surface reactivity can eventually be checked like in transmission infrared spectrometry for nanosized powders [7].

An important achievement of DRIFTS is to allow the analysis of the chemical reactions or interactions taking place at the very first atomic layer of a semiconductor layer simultaneously with their consequences on the electrical conductivity possibly involving a depth of few nanometers. Under those conditions, DRIFTS is an invaluable investigation tool in the field of chemical gas sensors for the comprehension of the fundamental mechanisms.

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